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BRIGHT BRASS SOLUTIONS

BY

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A THESIS SUBMITTED FOR THE DEGREE

OF

BACHELOR OF SCIENCE

COURSE IN CHEMICAL ENGINEERING

UNIVERSITY OF WISCONSIN

1917



## BRIGHT BRASS SOLUTIONS

In the electrolytic deposition of brass, the ordinary solution will give a dull or matte deposit, which must be polished in order to make it bright. This is true even when the article to be plated has a bright finish. It is therefore desirable to find a bath of such a composition that the alloy deposited will take the finish of the article which is being plated and will therefore need no subsequent polishing. Although this has been accomplished by the use of addition reagents, the literature on the subject is very limited. The electroplaters who have been able to deposit bright brass successfully regard their methods as great secrets and guard them accordingly. Consequently very little is known about the actual commercial methods for obtaining bright brass deposits.

The literature on the subject can be briefly summarized. In about a dozen books on electroplating only one or two mention a brightener for the brass bath. A. Roseleur<sup>1</sup> says that arsenious acid in a brass bath causes the deposit to be bright, but that too great an amount causes it to become white or gray. He further states that brass electroplaters say that arsenious acid cleans the bath because it is transformed into arsenic acid, thus preventing the deposits from containing the oxides of copper and zinc. The arsenites

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<sup>1</sup> A. Roseleur - Galvanoplastic Manipulations p.102.





of potassium, sodium, or ammonia, would be just as good, but double the quantities are needed. Several books mention arsenic as a constituent of brass baths and give the amount to be used, but say nothing of its purpose in the bath. Barclay and Hainsworth<sup>2</sup> mention arsenious acid, as do also H. H. Reama<sup>3</sup> and Wilh. Pfanhauser.<sup>4</sup> G. E. Bonney<sup>5</sup> includes arsenious acid as a constituent of one of a dozen formulas for brass solutions, and also calls attention to its brightening property. The editor of the Brass World<sup>6</sup> gives a method of adding arsenic to a brass bath. It consists simply of dissolving white arsenic in caustic potash and adding one or two ounces of arsenic to 100 gallons of solution. This article also states that "the caustic potash or soda added with the solution to the brass bath will have no effect on it". This, however, is contrary to an article by Alfred Martin.<sup>7</sup> He says that "one-half ounce of caustic potash in sticks to each gallon" will prevent the formation of the white film on the anode and also give a bright deposit.

Wilh. Pfanhauser discusses sodium carbonate as a brightener.<sup>8</sup> He says, "For small objects, chains etc., soda

<sup>2</sup> Electroplating, p. 352.

<sup>3</sup> Electroplating and Analysis of Solutions, p. 23.

<sup>4</sup> Elektro-Plattirung, p. 347.

<sup>5</sup> Electroplater's Handbook, p. 185 and 188.

<sup>6</sup> Brass World and Plater's Guide, 1909, p. 425.

<sup>7</sup> Brass World and Plater's Guide, 1909, p. 83.

<sup>8</sup> Elektro-Plattirung, p. 355.



(sodium carbonate) is often added to the bath in order to obtain a beautiful brilliant deposit with the same cell voltage". He has found, however, that the addition of the soda only raises the conductivity of the bath, and that by increasing the cell voltage, any good brass bath can be used for such articles as small chains, which have poor electrical contact.

The Brass World<sup>9</sup> claims that nickel carbonate as an addition reagent is much better than arsenic. The article states that much care is required when arsenic is used in order to prevent a pale or streaked deposit, whereas, if nickel carbonate is used less care is required and an excess does not injure the deposit. With a very large excess, however, the deposit is said to become pink.

A bright brass solution as given by W. T. Donnelly<sup>10</sup> consists of an ordinary cyanide bath to which is added the "brightening stock solution". This is made by adding one-half ounce of white arsenic to two ounces of carbon bisulphide and two and one-half ounces of chloroform. This is made up to one gallon with the brass solution, which contains one-half ounce of ammonia to each gallon. One ounce of the stock solution should be added to each 100 gallons of brass solution every night.

Bi-sulphite of soda and ammonia are often added to brass baths. Although ammonia acts as a temporary brightener, its chief use in the brass bath is to dissolve the precipi-

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<sup>9</sup> Brass World and Plater's Guide, 1914, p. 22.

<sup>10</sup> Brass World and Plater's Guide, 1909, p. 54.



tates.<sup>11</sup>

In order to experiment with some of the substances recommended as brighteners it was first necessary to make a brass bath which would give a satisfactory color. Ordinarily a brass bath is considered to be one of the most difficult electrolytic baths to control. Although there are many different kinds of baths possible the cyanide bath is now used entirely. Brass plating was first carried out by means of a cyanide bath by Ruolz in 1842, but it was not introduced into practice for some time on account of the high cost.<sup>12</sup> However, it cannot be considered to be entirely satisfactory even now. The chief objections seem to be that it is slow and that discoloration in spots is likely to appear after the surface has been polished and lacquered. The bath as it is usually made up consists of potassium zinc cyanide and potassium copper cyanide with a small excess of potassium cyanide.<sup>13</sup> Cast brass anodes are used, and the current density used in most baths is about 0.3 amperes per square decimeter. The color of the brass deposited can be controlled by the addition of cyanide of zinc or copper, and by varying the temperature of the solution or the voltage used.<sup>14</sup> Therefore it would be a difficult matter to specify a definite composition for a brass bath. Probably the best way to make up a solution is to use the

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<sup>11</sup> G. E. Bonney - Electroplaters Handbook, p. 186.

<sup>12</sup> M. deKay Thompson - Metallurgical & Chemical Eng., 10, p. 458.

<sup>13</sup> Hogsboom - Tr. A. E. S., 19, p. 53-56.

<sup>14</sup> Brass World and Plater's Guide, July 1916, p. 209.



amounts of chemicals which will give approximately the desired composition, and then additions can be made later to get the desired color of deposit.





## EXPERIMENTS

A brass solution was first made.<sup>15</sup> After the sodium cyanide had been dissolved in water the carbonates of zinc and copper were added, and the solution was warmed. It was then filtered, diluted to about two liters, and ammonia was added. The amounts of the chemicals used were:-

NaCN	55	grams
ZnCO <sub>3</sub>	7	"
CuCO <sub>3</sub>	43	"
NH <sub>4</sub> OH	7	"

On testing this bath it was found that more zinc carbonate was needed in order to obtain a good yellow colored deposit. Zinc carbonate was therefore added until the desired color of brass was obtained, with a current density of about 0.3 amperes per square decimeter. This bath was used in portions of about 300 cc. each for trying the various addition reagents. At first only one cell was used. It was connected to a 10 volt circuit with an ammeter, rheostat, and switch in series. Using current densities ranging from 0.15 amperes to 0.5 amperes per square decimeter the current was passed for three minutes using increasing amounts of the addition reagent in the bath. Tinned cathodes were used. These tests, however, were of no value because the brass coating obtained was too thin for any

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<sup>15</sup> W. T. Donnelly - Brass World and Plater's Guide, 1909, p.54.



practical use. Therefore the tests were run for a longer time in order to get a heavier deposit. Also two and sometimes three cells were connected in series in order to save time. This also served as a means of comparing the deposits obtained with and without addition reagents. Most of the tests were run for thirty minutes unless it became obvious before that length of time that a particular experiment was a failure. It became necessary from time to time to replenish the solutions with cyanide or zinc carbonate in order to keep them in good working condition. With too little free cyanide the anode corrosion was poor and an insulating film was formed on the anodes which cut down the flow of current and consequently caused a thin deposit and a variation in the color of the deposit. Too much free cyanide would also cause a thin deposit. However, the size of the bath used might have been a factor in bringing about the difficulties mentioned above. The zinc and copper are not exhausted from the bath in the same proportion, neither are they replenished in the same proportions as deposited, and in a small solution it would probably not take long to change the composition enough so that a different colored deposit would be made. Such a change would be more gradual in a large bath.

The first addition reagent used was arsenic, in the form of sodium arsenate,  $\text{Na}_3\text{AsO}_4 \cdot 12\text{H}_2\text{O}$ . According to the literature on the subject it should be added in very small amounts. Therefore a solution of one gram in 200 cc. of water was made, and the additions were made as shown in the data.



TABLE I.

Addition reagent:- 1 gm.  $\text{Na}_3\text{AsO}_4 \cdot 12\text{H}_2\text{O}$  in 200 cc. of water.

No.	Time Min.	Amps. per dcm. <sup>2</sup>	Addition Reagent cc.	Remarks on Deposit Color	Surface
1.	3	0.4	1	Yellow	Bright
2.	20	0.4	1	Yellow	Began to get dull
3.	20	0.25	2	Yellow	Dull brown spots
4.	32	0.17	2	Pink	Bright
5.	32	0.17	3	Yellow	Bright, but thin
6.	30	0.3	3	Yellow	Bright, non-adherent
7.	30	0.6-0.2	3	Yellow	Bright, non-adherent
8.	20	0.8	3	Pink, after polishing	Matte
9.	30	0.3	3	Yellow	Bright
10.	35	0.5-0.2	4	Yellow	Bright, non-adherent
11.	60	0.3-0.07	4	Pink	Bright
12.	30	0.3-0.15	6	Yellow	Very bright, thin
13.	10	0.6	6	Brown	Matte, non-adherent
14.	30	0.25	6	Brown	Matte
15.	30	0.3-0.15	6	Yellow	Bright
16.	30	0.3	7	Yellow	Began to get streaked
17.	22	0.5	7	Dull yellow	Streaked, peeled off
18.	25	0.3	10	Yellow	Streaked, matte
19.	30	0.4	10	Yellow	Streaked near edges
20.	10	0.35	10	Yellow	Streaked deposit



The preceding experiments were made at room temperature. Following are the results obtained in a warm solution:-

No.	Time Min.	Amps. per dcm. <sup>2</sup>	Addition Reagent cc.	Temp. C.	Remarks on deposit Color	Surface
21.	10	0.6	3	42	Copper	Dull
22.	35	0.3	3	42	Copper	Bright
23.	12	0.6	3	42	Copper	Bright
24.	10	1.7-1.0	4	46	Copper	Dull
25.	10	0.7	4	46	Copper	Dull
26.	10	0.3	4	46	Copper	Dull

Specimen number 5, which was run for 32 minutes with a current density of 0.17 amperes per square decimeter, had a bright yellow deposit but it was very thin. The bath contained 3 cc. of the addition reagent.

Specimen number 6 was produced in the same bath with a current density of 0.3 amperes per square decimeter for thirty minutes. The deposit was a very bright yellow brass, but it came off under the action of the scratch brush. It is probable, however, that this was due to insufficient cleaning of the tinned cathode.

Specimen number 9 was probably the most satisfactory. It had a good bright brass deposit which was produced at a density of 0.3 amperes per square decimeter for thirty minutes





with 3 cc. of addition reagent in the bath. Another case in which a bright brass was obtained was specimen number 12. The bath contained 6 cc. of the addition reagent and although the current was passed for 30 minutes the density dropped from 0.3 to 0.15 amperes per square decimeter. Therefore the deposit was probably not very thick. With further additions of the addition reagent there was no improvement in the kind of deposit obtained. The best results were obtained with 3 cc. of the addition reagent in the bath, the volume of which was 300 cc. This amounts to 0.05 grams of sodium arsenate per liter of solution.

The results obtained in the warm solution will be discussed later.

Nickel carbonate was another addition reagent used.<sup>16</sup> This was made by adding sodium carbonate to a warm solution of nickel chloride. The water was decanted from the green precipitate, which was washed several times with hot water and filtered. This precipitate of nickel carbonate was then dissolved in a portion of the brass bath and was added to the plating solution in this form. The prescribed amount to use was one pint of plastic nickel carbonate to 100 gallons of solution. The reagent as it was used contained about one part by volume of the plastic nickel carbonate to ten parts by volume of the reagent. Therefore, by adding one or two cubic centimeters at a time the amount of addition reagent used was varied from less than the prescribed amount to an amount ex-

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<sup>16</sup> Brass World and Plater's Guide, 1914, p. 22.



ceeding that prescribed. Most of the experiments were run for thirty minutes with a current density of about 0.3 amperes per square decimeter. Several tests, however, were run with a density as high as 0.6 amperes per square decimeter. All of the tests were run at room temperature. Fifteen different tests were tried with this reagent, but no bright brass was obtained. There was no apparent difference between the deposits obtained from this bath and those obtained from a bath without addition reagents, except that the color of the matte formed on the deposit became darker with increasing amounts of addition reagent. The color changed from pink with the first few additions, to brown when the experiments were discontinued.



TABLE II.

Addition reagent:- Nickel carbonate.

No.	Time Min.	Amps. per dcm. <sup>2</sup>	Addition Reagent cc.	Remarks on Deposit Color	Surface
27.	30	0.3	1	Yellow	Dull
28.	30	0.3	1	Streaked deposit	
29.	30	0.6	1	Streaked deposit	
30.	30	0.3	1	Pink	Matte deposit
31.	30	0.3	2	Pink	Matte deposit
32.	30	0.6-0.4	2	Pink	Matte deposit
33.	20	0.4	2	Red	Matte deposit, polished to copper color
34.	30	0.3	4	Red	Matte deposit
35.	30	0.3	5	Red	Matte deposit
36.	30	0.3	5	Brown	Matte deposit, non-adherent
37.	30	0.3	7	Brown	Matte deposit, at center
38.	10	0.6	7	Brown	Matte deposit
39.	30	0.3	9	Brown	Matte deposit
40.	30	0.3	11	Brown	Matte deposit

A very interesting addition reagent<sup>17</sup> was one composed of 0.5 grams of arsenious oxide, 25 cc. of chloroform,

<sup>17</sup> Brass World, 1909, p. 54.



and 25 cc. of carbon bisulphide. This was made up to 225 cc. with a portion of the brass bath. Small amounts of the reagent were added and experiments were made with current densities varying from 0.15 to 0.8 amperes per square decimeter. A peculiar thing about this bath was the fact that it seemed to be necessary for it to stand at least 48 hours after the addition of the reagent, before a good deposit could be obtained.

When the bath was used immediately after the addition of the reagent, the deposit obtained was iridescent. After the bath had stood for about 24 hours a copper colored deposit was obtained which gradually changed to iridescence. After two days, however, the brass deposit was of a very good yellow color.

Bright yellow deposits were obtained with current densities varying from 0.20 to 0.50 amperes per square decimeter. With these specimens, numbers 46 and 47, the current was passed for 30 minutes and the addition reagent used amounted to two cc. in 300 cc. of the bath. Although the deposits were non-adherent, it was probably due to the fact that the tinned cathodes were not thoroughly cleaned. Current densities up to 0.8 amperes per square decimeter were tried but the deposits were spotted and non-adherent. Specimen number 51 had a satisfactory, adherent, bright brass deposit, which was obtained from this bath with 3 cc. of the addition reagent using a current density of 0.3 amperes per square decimeter for 30 minutes at room temperature. This was the best deposit obtained. With further additions of the reagent the deposits obtained were dull. None of the deposits made in the warmed solution were bright.





TABLE III.

Addition reagent:- Chloroform - 25 cc.

Carbon bisulphide - 25 cc.

Arsenious oxide - 0.5 gm.

Made up to 225 cc. with brass solution.

No.	Time Min.	Amps. per dm. <sup>2</sup>	Addition Reagent cc.	Remarks on Deposit Color	Surface
41.	32	0.15	2	Iridescent	
42.	30	0.30	2	Iridescent	Streaked
43.	30	0.6-0.2	2	Yellow	Dull
44.	20	0.8	2	Yellow	Bright with dull spots at center
45.	15	0.7	2	Brown spots in middle, non- adherent	
46.	30	0.3	2	Yellow	Bright, non- adherent
47.	35	0.5-0.2	2	Yellow.	Bright, non- adherent
48.	60	0.3-0.07	2	Part dull and part bright yellow	
49.	30	0.3-0.2	3	Iridescent	
50.	30	0.3-0.15	3	Copper, changed to iridescent on exposure	
51.	30	0.3	3	Yellow	Bright
52.	28	0.6	3	Yellow	Dull
53.	22	0.6	3	Yellow	Dull
54.	30	0.3	5	Yellow	Dull
55.	20	0.6	5	Gray	Matte deposit
56.	30	0.3	5	Streaked deposit	



The above tests were all made at room temperature.  
Below are listed a few tests made with warmed solutions:-

No.	Time Min.	Amps. per dec. <sup>2</sup>	Addition Reagent cc.	Temp. C.	Remarks on Deposit Color	Surface
57.	35	0.3	2	42	Copper	Dull brown spots
58.	12	0.6	2	42	Copper	Dull brown spots
59.	10	1.7-1.0	2	44-47	Copper	Dull
60.	10	0.7	2	58	Copper	Dull
61.	10	0.3	2	58	Copper	Dull

In practically all of the tests a cell containing the ordinary brass bath without reagents was run in series with one or more of the others. It was found that when this bath was new, the deposit obtained was bright. This was thought to be due to the brightening property of the ammonia which is said to be a temporary brightener.<sup>18</sup> After the bath had been in use for some time a few drops of ammonia were added and immediately a bright brass was obtained. This deposit, specimen number 70, was obtained with a current density of 0.3 amperes per square decimeter for thirty minutes at room temperature. After the bath had been in use for a while it again gave a matte deposit, which would indicate that the ammonia had a temporary brightening effect.

The effect of heating the solution was tried on all

<sup>18</sup> Brass World, July 1916, p. 209, Q. & A. #308.



of the baths except the one containing the nickel carbonate addition reagent. The temperatures used range from about 40° C. to 60° C. The deposits were all copper colored.

The explanation is that the increase in temperature increases the mobility of the bath, and therefore has the same effect as stirring, which causes the deposition of a smaller proportion of the more electro-positive metal, zinc.<sup>19</sup>

Only a few tests were made with a warmed solution, because no brass colored deposits were obtained. One specimen, number 84, having a bright copper deposit, was obtained in the solution without addition reagents, by passing a current of 0.3 amperes per square decimeter for thirty-five minutes. The temperature of the bath was 42° C. In the solution containing 3 cc. of the sodium arsenate reagent, which was connected in series with the above mentioned bath, a bright copper deposit was obtained (specimen number 22). Another specimen (number 23) of bright copper was obtained in the same bath at a density of 0.6 amperes per square decimeter, yet specimen number 21 which was made under almost identical conditions had a dull deposit. Because of these contradictory results and the small number of tests made, the data obtained does not warrant any conclusions in regard to the use of addition reagents in a warm solution.

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<sup>19</sup> O. P. Watts - Laboratory Course in Electroplating, p. 99.



TABLE IV.

No Addition Reagent			
No.	Time Min.	Amps. per dec. <sup>2</sup>	Remarks on deposit Color Surface
62.	3	0.4	Bright deposit
63.	20	0.4	Red streaked deposit
64.	20	0.27	Brown Matte deposit
65.	32	0.17	Yellow Bright deposit
66.	32	0.17	Yellow Bright deposit
67.	30	0.25	Yellow Dull deposit
68.	30	0.6-0.2	Yellow Dull deposit
69.	20	0.75	Matte, ploished to copper color
70.	30	0.30	Yellow Bright
			Made after addition of ammonia
71.	35	0.4-0.12	Yellow Bright, non-adherent
72.	30	0.3-0.15	Yellow Fairly bright, but thin
73.	10	0.6	Brown film
74.	30	0.3-0.25	Matte, non-adherent
75.	30	0.3-0.15	Streaked deposit
76.	30	0.3	Brown Streaked deposit
77.	22	0.6	Streaked dull gray, polished to good color
78.	22	0.8-0.48	Matte deposit, polished to good color
79.	25	0.3	Matte, streaked, polished to good color
80.	30	0.3	Matte deposit
81.	10	0.6	Matte deposit
82.	30	0.25	Matte deposit





The above deposits were made at room temperature (21°C.). Below are a few tests made with a warmed solution:-

No.	Time Min.	Amps. per dec. <sup>2</sup>	Temp. C.	Remarks on Deposit Color	Surface
83.	10	0.6	42	Copper colored	Dull
84.	35	0.30	42	Copper colored	Bright
85.	12	0.6	42	Copper colored	Matte
86.	10	1.7-1.0	45	Copper colored	Dull
87.	10	0.7	58	Copper colored	Dull
88.	10	0.3	58	Copper colored	Dull

TABLE V.

## No Addition Reagent

No.	Time Min.	Amps. per dec. <sup>2</sup>	Remarks on Deposit Color	Surface
89.	30	0.3	New Solution--	Good bright brass
90.	30	0.6-0.4	Good bright brass	
91.	20	0.4		Matte deposit
92.	30	0.3		Matte deposit
93.	20	0.6		Matte deposit
94.	30	0.3		Matte deposit
95.	10	0.35	Brown streaks	Matte deposit
96.	30	0.3	Brown	Matte deposit
97.	30	0.3	Brown	Matte deposit
98.	10	0.6		Matte deposit
99.	30	0.3	Brown	Matte deposit



## CONCLUSIONS

The results obtained in this work indicate that:-

1. Sodium arsenate, if added to a brass bath in very small quantities (0.05 gm. per liter) causes the deposition to be bright, provided, of course, that the bath is operated under the proper conditions for depositing brass.

2. The addition reagent consisting of 25 cc. of carbon bisulphide, 25 cc. of chloroform, 0.5 gm. of white arsenic, and enough brass solution to make the volume 225 cc. causes the deposit to be bright if the bath is allowed to stand idle for a few days after the reagent has been added. If a deposit is made before that time, it will appear iridescent. The amount of reagent which gave the best results was 10 cc. per liter of brass solution.

3. Nickel carbonate as an addition reagent had no effect as a brightener within the limits in which it was used in this work.

4. Ammonia acts as a temporary brightener.



Approved:

Oliver P. Watts.

Assist. Prof. of  
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June 12, 1917.















































































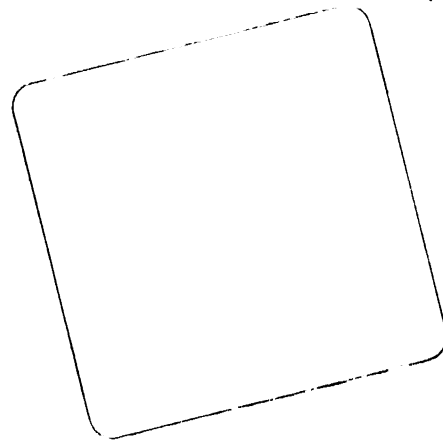




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